

## Appendix R. Laboratory Audit Results and Response



Paul E. Helliker  
Director

# Department of Pesticide Regulation



Gray Davis  
Governor

Winston H. Hickox  
Secretary, California  
Environmental  
Protection Agency

## MEMORANDUM

TO: Don Fitzell  
Quality Assurance Section  
Monitoring & Laboratory Division  
Air Resources Board  
1927 13<sup>th</sup> Street  
Sacramento, California 95814

FROM: Randy Segawa, Senior Environmental Research Scientist  
Environmental Monitoring and  
Pest Management Branch

DATE: May 22, 2000

SUBJECT: RESULTS OF PRE-STUDY AUDIT OF UNIVERSITY OF CALIFORNIA  
DAVIS' TRACE ANALYTICAL LABORATORY

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We received your results from the Quality Assurance audit team that conducted a pre-study evaluation of the University of California Davis' Trace Analytical Laboratory (TAL) on May 12, 2000, to evaluate the readiness of the laboratory to start analyzing samples from the Lompoc Phase II monitoring. Another outstanding job by the Quality Assurance (QA) team! In particular, thank you for fitting this activity into your busy schedules.

We will make the appropriate arrangements and changes, and respond to your findings before the start of monitoring. We were pleased to hear that, overall, you found that the lab's preparations and procedures appear to be in order. You identified the following questions to resolve before the start of sampling. Our answers follow each of the questions you posed.

**1—It is unclear to TAL how samples will be shipped from Lompoc. If UPS is used, since UPS does not deliver samples on weekends, samples should be kept on dry ice by the Lompoc technician over the weekend and then shipped on the following Monday, to prevent the samples sitting somewhere in a UPS warehouse and getting warm. DPR will ship samples overnight from Lompoc by FedEx.**

**2—It is unclear whether the primary samples for TAL and the duplicates for the Department of Food and Agriculture (DFA) lab will be sent to Sacramento or Davis in one chest, or a separate ice chest to each lab with separate chain of custody forms. If primary and duplicates are shipped together, the Lompoc technician should be instructed to group samples by lab with separate chain of custody forms, and clearly mark which samples are for which lab.**

The primary samples for TAG and the duplicates for the DFA lab will be sent to Sacramento in separate ice chests, and each lab will have separate chain of custody forms. Staff from each laboratory will pick up its respective samples from the Sacramento airport.



**3—Samples should be shipped in individual sealed plastic bags each containing a label for the individual sample.**

The Lompoc technician will ship samples in individual sealed plastic bags each containing a label for the individual sample, as suggested.

**4—Primary and back-up contacts at DPR should be identified, along with phone numbers, in the DPR Sampling and Analysis Plan.**

DPR will make these changes.

**5—The field technician should be instructed to use permanent ink on chain of custody forms, to avoid the smudging of ink due to the forms getting wet in the ice chests.**

DPR will instruct the field technician to use permanent ink on chain of custody forms.

**6—Upon shipping samples from Lompoc to Northern California, the Lompoc technician should be asked to fax a sample list to TAL at (530) 754-8556 and to DPR (and the DFA lab, if desired) to alert the TAL of the number of samples being shipped.**

DPR will ask the Lompoc technician to fax a sample list to TAL and to DPR at (916) 324-4088 (and the DFA lab at (916) 262-1434) to alert the TAL, upon shipping samples from Lompoc, of the number of samples being shipped.

**7—DPR should state in the Sampling and Analysis Plan and inform TAL how samples will be identified that will require analysis for oxydemeton-methyl.**

Samples that require analysis for oxydemeton-methyl will be in separate plastic bags, labeled oxydemeton-methyl. DPR will state this in the Sampling and Analysis Plan and inform TAL.

**8—TAL should provide DPR with final analytical standard operating procedures for incorporation by DPR in the Sampling and Analysis Plan.**

TAL has provided DPR with final analytical standard operating procedures and DPR will incorporate them in the Sampling and Analysis Plan.

**9—The TAL and DFA labs will exchange standards for the four pesticides that the DFA lab will analyze in duplicate samples. The date of the exchange of standards and a date by which the labs are to report results to DPR should be known to both labs. Once both labs report results of the analysis of the other lab's standards to DPR, DPR should provide these results to both labs and the QA team.**

DPR has discussed this exchange of standards with both the TAL and the DFA lab. DPR, TAL and DFA labs have agreed that all three parties should know the date of the exchange of standards and a date by which the labs are to report results to DPR. DPR is in the process of scheduling the date of the exchange of standards, and the date by which labs are to report results

Don Fitzell  
May 22, 2000  
Page 3

to DPR, and will provide all parties these dates. When DPR has both labs' report results of the analysis of the other lab's standards, DPR will provide these results to both labs and the QA team. This process will be described in the final Sampling and Analysis Plan.

If you have any questions or comments about these responses, please feel free to contact me by telephone at (916) 324-4137 or by e-mail at <rsegawa@cdpr.ca.gov>.

cc: Lynn Baker, ARB  
Kathy Orr, DPR  
Matt Plate, U.S. EPA  
Susan Kegley, PAN  
Cathy Cooper, CDFA  
Matt Hengel, UCD TAL  
Dave Vener, Xontech  
Carissa Ganapathy, DPR  
Pam Wofford, DPR  
Madeline Brattesani, DPR  
TAG members



Winston H. Hickox  
Agency Secretary

# Air Resources Board

Alan C. Lloyd, Ph.D.  
Chairman

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Gray Davis  
Governor

## MEMORANDUM

TO: Randy Segawa  
Senior Environmental Scientist  
Environmental Monitoring and Pest Management Branch  
Department of Pesticide Regulation

FROM: *N2*  
*for MM* Michael Miguel, Manager  
Quality Assurance Section  
Monitoring and Laboratory Division

DATE: June 12, 2000

SUBJECT: EVALUATION OF UC DAVIS LABORATORY PRIOR TO LOMPOC  
PHASE II MONITORING

On May 12, 2000, the Quality Assurance (QA) team completed its pre-monitoring, on-site evaluation of the Trace Analysis Laboratory (TAL) at the University of California, Davis. The QA team consisted of: Don Fitzell of the Air Resources Board (ARB), Mathew Plate of the United States Environmental Protection Agency (U.S. EPA), Kathy Orr of the Department of Pesticide Regulation (DPR), Susan Kegley of the Pesticide Action Network, and Lynn Baker of the ARB.

The team met with Matt Hengel, Mike McChesney, and Greg Hall of the TAL. Overall, the laboratory had all appropriate quality assurance/quality control (QA/QC) procedures in place. No significant deficiencies were observed. On May 15, 2000, Lynn Baker sent you an e-mail with several questions that needed to be resolved prior to the start of monitoring. On May 22, 2000, the QA team received your responses to these questions (attached). All questions were satisfactorily answered by the DPR. After the QA audit team further reviewed its notes, some members had additional observations that it felt should be brought to your attention. Those comments are listed below:

- 1) Due to the varying responses of the pesticides analyzed, the TAL does not have stringent, quantifiable QC criteria for such things as: calibration linearity, precision of duplicate samples, or instrument sensitivity. In future sampling plans the DPR should make clear those criteria sensitive to the study's goals and specify to the TAL corrective action required such as: qualifying the data, invalidating the data or re-analyzing samples/extracts when criteria are not met.

2) In some cases the pesticides being analyzed have a linear range which goes below the quantitation limit being reported. The TAL felt this was necessary due to the number of pesticides being analyzed at one time. If the DPR has interest in the lower levels of these pesticides or similar pesticides in future studies, the TAL should be notified prior to the start of the study.

3) The TAL reports a trapping efficiency recovery level of 37% for cycloate. The DPR should be aware that this could affect samples reported as trace (detected but not quantifiable) as well as reported values. As a result, a very conservative risk assessment should be considered regarding exposure to trace levels of cycloate.

4) Sample extracts are potentially left sitting for long periods at room temperature while awaiting analysis in autosampler trays. This is to accommodate analytical runs that are one to three days in length. The TAL intersperses detection limit checks throughout their analytical runs, including one at or near the end of the run. The DPR should be aware of this and any corrective action taken by the TAL due to pesticide degradation or solvent loss.

5) Most trapping efficiencies were determined from literature or previous in-house studies. Trapping efficiency studies were conducted for six pesticides for which no previous trapping efficiency data existed. All six pesticides were simultaneously fortified onto four replicate XAD-4 sampling tubes. The trapping efficiency study was conducted indoors. No breakthrough was detected. DPR should be aware that recovery studies have not been conducted for all of the target analytes simultaneously spiked to the same sampling tubes. Although this is not expected to pose a significant analytical problem, field spikes from Lompoc should address this potential shortcoming. In future studies, if the DPR is concerned with possible interaction between target pesticides, it should instruct the TAL that trapping efficiency studies be conducted for all target analytes simultaneously, and that such studies be conducted under representative or expected field conditions.

If you have questions regarding these comments, please call me at (916) 324-6191 or Don Fitzell at (916) 322-3892.

Attachment

Randy Segawa  
June 12, 2000  
Page 3

cc: Matt Hengel, UC Davis  
Don Fitzell, ARB-MLD  
Mathew Plate, U.S. EPA Region IX  
Kathy Orr, DPR  
Susan Kegley, Pesticide Action Network  
Lynn Baker, ARB-SSD



**Winston H. Hickox**  
Agency Secretary

# Air Resources Board

**Alan C. Lloyd, Ph.D.**  
Chairman

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**Gray Davis**  
Governor

## MEMORANDUM

**TO:** Randy Segawa  
Senior Environmental Scientist  
Environmental Monitoring and Pest Management Branch  
Department of Pesticide Regulation

**FROM:** Michael Miguel, Manager //s//  
Quality Assurance Section  
Monitoring and Laboratory Division

**DATE:** July 28, 2000

**SUBJECT:** PRELIMINARY REPORT OF SYSTEMS AUDIT OF UCD-TAL AND CDFA LABORATORIES

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The purpose of this preliminary report is to provide a summary of the system audits' findings for the UC Davis Trace Analytical Laboratory (TAL) and the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry. This preliminary report will enable the Department of Pesticide Regulation (DPR) to modify procedures where necessary. A full report will be issued at a later date.

On July 24, 2000, the Quality Assurance team evaluated the UC Davis TAL, which is analyzing the ambient samples, and the CDFA laboratory in Sacramento, which is analyzing collocated samples for the Lompoc pesticide study.

Both laboratories were following accepted and agreed-upon procedures for analysis and quality assurance, including sample handling, instrument calibration, method validation, and documentation. As a result of the system audits, the audit team is informing the Department of Pesticide Regulation (DPR) of two issues:

- 1) At the UC Davis TAL, there is uncertainty for some pesticides reported as trace or not detected. The audit team will provide the DPR with recommended options regarding this issue. The recommendations will be included in the full audit report.
- 2) At the CDFA laboratory, at least two batches of samples have been received without dry ice present in the ice chest. Lynn Baker has already informed the DPR of this problem. The audit team recommends: a) the field technician place more dry ice in the chest for the CDFA lab and use a larger ice chest if



Randy Segawa  
July 28, 2000  
Page 2

necessary, and b) include a trip blank and trip spike with the samples so recovery levels can be corrected if samples become too warm.

Other issues were discussed among the audit team, none of which would significantly affect data quality. These issues will be addressed in the full report.

cc: Cathrine Cooper, CDFA Laboratory  
Matt Hengel, UC Davis  
Susan Kegley, Pesticide Action Network  
Mathew Plate, US EPA  
Kathy Orr, DPR  
Lynn Baker, ARB  
Don Fitzell, ARB



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Gray Davis  
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## MEMORANDUM

TO: Randy Segawa  
Senior Environmental Scientist  
Environmental Monitoring and Pest Management Branch  
Department of Pesticide Regulation

FROM: Michael Miguel, Manager *MS Miguel*  
Quality Assurance Section  
Monitoring and Laboratory Division

DATE: September 8, 2000

SUBJECT: FINAL REPORT OF SYSTEM AUDITS OF UCD-TAL AND CDFA  
LABORATORIES - LOMPOC PHASE II MONITORING

This report summarizes the system audit findings for the UC Davis Trace Analytical Laboratory (TAL) and the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry. A preliminary report was sent to the Department of Pesticide Regulation (DPR) after the audits were conducted on July 24, 2000.

The Quality Assurance (QA) team evaluated the TAL, which analyzes the ambient samples, (including some collocated for laboratory precision) and the CDFA laboratory in Sacramento, which analyzes other collocated samples used to evaluate the accuracy of the TAL, for the Lompoc pesticide study.

Both laboratories were following accepted and agreed-upon procedures for analysis and quality assurance, including sample handling, instrument calibration, method validation, and documentation. The QA audit team had the following comments and recommendations for the TAL, the CDFA laboratory, and the DPR:

### TAL

1. There is uncertainty for some pesticides reported as trace or not detected. The calibration curves produced by the Mass Selective Detector (MSD) and the Flame Photometric Detector (FPD) had both positive Y-intercepts and negative Y-intercepts, for some of the runs. This may have resulted in under reporting of pesticides with negative Y-intercepts (trace levels reported as non-detected) and over-reporting of pesticides with positive Y-intercepts (non-

detected levels reported as trace). The QA team suggests three possible ways of resolving with this situation:

- 1) Request the TAL to reevaluate the data by looking at each chromatogram individually to ensure accuracy.
  - 2) For purposes of exposure and risk assessment, set the concentration for all trace and non-detects at the midpoint between the Method Detection Limit (MDL) and the Estimated Quantitation Limit (EQL); if needed, evaluate data more closely for specific analytes.
  - 3) Use the data as reported by the TAL with a detailed note clarifying these uncertainties.
2. The TAL used a calibration standard for analysis of fonofos samples that was past its expiration date. The laboratory did attempt to replace the standard, but was unsuccessful. The TAL did verify that the standard did not degrade from prior use. The QA team does not feel that this is a problem.

#### CDFA Laboratory

1. As noted in the preliminary report, the CDFA laboratory received at least two batches of samples without dry ice present in the ice chest. In future studies, the audit team recommends: a) the field technician use an ice chest large enough to accommodate the samples and sufficient dry ice to maintain the temperature until received at the laboratory, and b) the study design should include a trip blank and trip spike with all samples so recovery levels can be corrected if samples become too warm.
2. The CDFA laboratory still does not have a formal data review process. Normally, the data are reviewed by another CDFA analytical chemist and the supervising chemist.
3. The CDFA laboratory was requested by the DPR to report values below their EQL in order to confirm results by the TAL, which had lower detection limits. The lead chemist included standards at this lower level in calibration curves. The QA team feels this was an excellent QA solution.

#### The DPR

1. The samples shipped from Lompoc on July 21, 2000, to the TAL were mis-routed by Federal Express and did not reach the laboratory until the following Monday, July 24. No dry ice was present and the samples were at room temperature. The trip spike was analyzed and all recoveries were acceptable except for chlorothalonil (47%) and naled (62%). This should be noted in the DPR final report.

2. More than one batch of samples shipped to the CDFA laboratory were received without dry ice present in the container. These results should be identified and noted in the DPR final report.
3. Some documentation prepared by the DPR regarding the sampling and analysis plan was not provided to all members of the QA audit team. This complicated the evaluation of certain laboratory procedures, specifically whether certain procedures were consistent with the laboratory's contractual responsibilities. When questions arose, some QA team members had difficulty obtaining the information necessary to conduct an informed evaluation of the QA procedures.
4. During the Lompoc Phase II monitoring, samples were collected using XAD-4 resin cartridges. The QA audit team understands that members of the Lompoc Interagency Work Group raised questions about whether or not particulate matter with adsorbed pesticides might be passing through the resin sampling cartridges. At the DPR's direction, some collocated XAD-4 samplers were operated with and without filters to evaluate the collection efficiency of the primary sampling method. The TAL analyzed the XAD and filter samples for this comparison. This comparison was conducted after the audit of the TAL. The DPR final report should note that this aspect of the TAL analysis was not reviewed by the QA team.

cc: Catherine Cooper, CDFA Laboratory  
Matt Hengel, UC Davis  
Susan Kegley, Ph.D., Pesticide Action Network  
Matthew Plate, U.S. EPA Region IX  
Kathy Orr, DPR  
Lynn Baker, ARB  
Don Fitzell, ARB



Paul E. Helliker  
Director

# Department of Pesticide Regulation



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Environmental  
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## MEMORANDUM

TO: Michael Miguel, Manager  
Air Resources Board  
Monitoring and Laboratory Division  
Quality Assurance Section  
2020 L Street  
Sacramento, California 95814

FROM: Randy Segawa, Senior Environmental Research Scientist  
Environmental Monitoring and  
Pest Management Branch  
(916) 324-4137

*Segawa*

DATE: October 10, 2000

SUBJECT: RESPONSE TO LOMPOC PHASE 2 AUDIT

Thank you for the report on the quality assurance (QA) audit for the laboratories conducting the Lompoc Phase 2 analyses. As usual, the report is very useful. The following responds to your specific findings.

### Trace Analytical Laboratory (TAL)

1. There is uncertainty for some pesticides reported as trace or not detected. The calibration curves produced by the Mass Selective Detector (MSD) and the Flame Photometric Detector (FPD) had both positive Y-intercepts and negative Y-intercepts, for some of the runs. This may have resulted in under reporting of pesticides with negative Y-intercepts (trace levels reported as non-detected) and over-reporting of pesticides with positive Y-intercepts (non-detected levels reported as trace). The QA team suggests three possible ways of resolving this situation:

Response: The Department of Pesticide Regulation (DPR) will implement option 2 and part of option 3. For exposure assessment purposes, DPR will set the concentration for all trace and non-detects at the midpoint between the method detection limit and the estimated quantitation limit. DPR will also include a detailed description clarifying the uncertainties of the trace and non-detects. DPR believes that there is little gain to reevaluating each chromatogram (option 1), since the estimated quantitation limits for most analytes are at least 10 times lower than the health screening level.



2. The TAL used a calibration standard for analysis of fonofos that was past its expiration date. The laboratory did attempt to replace the standard, but was unsuccessful.

Response: The TAL discussed the fonofos standard with DPR prior to its expiration. DPR concurs with the TAL and QA team that subsequent analyses indicate this is not a problem.

#### **California Department of Food and Agriculture (CDFA) Laboratory**

1. As noted in the preliminary report, the CDFA laboratory received at least two batches of samples without dry ice present in the ice chest. In future studies, the audit team recommends; a) the field technician use an ice chest large enough to accommodate the samples and sufficient dry ice to maintain the temperature until received at the laboratory, and b) the study design should include a trip blank and trip spike with all samples so recovery levels can be corrected if samples become too warm.

Response: DPR concurs with the QA team's recommendation.

2. The CDFA laboratory still does not have a formal data review process. Normally, the data are reviewed by another CDFA analytical chemist and the supervising chemist.

Response: DPR will request that CDFA develop a standard operating procedure for data review.

#### **DPR**

1. The samples shipped from Lompoc on July 21, 2000, to the TAL were mis-routed by Federal Express and did not reach the laboratory until the following Monday, July 24. No dry ice was present and the samples were at room temperature. The trip spike was analyzed and all recoveries were acceptable except chlorothalonil (47%) and naled (62%). This should be noted in the DPR final report.

Response: The samples to CDFA were also mis-routed. DPR concurs with the recommendation.

2. More than one batch of samples shipped to the CDFA laboratory were received without dry ice present in the container. These results should be identified and noted in the DPR final report.

Response: DPR concurs with the recommendation.

3. Some documentation prepared by DPR regarding the sampling and analysis plan was not provided to all members of the QA audit team. This complicated the evaluation of certain laboratory procedures, specifically whether certain procedures were consistent with the laboratory's contractual responsibilities. When questions arose, some QA team members had difficulty obtaining the information necessary to conduct an informed evaluation of the QA procedures.

Response: DPR will provide all documentation to all QA team members in the future.

4. During the Lompoc Phase II monitoring, samples were collected using XAD-4 resin cartridges. The QA audit team understands that members of the Lompoc Interagency Work Group raised questions about whether or not particulate matter with adsorbed pesticides might be passing through the resin sampling cartridges. At the DPR's direction, some collocated XAD-4 samplers were operated with and without filters to evaluate the collection efficiency of the primary sampling method. The TAL analyzed the XAD and filter samples for this comparison. This comparison was conducted after the audit of the TAL. The DPR final report should note that this aspect of the TAL analysis was not reviewed by the QA team.

Response: DPR concurs with the recommendation. Due to the timing of the analysis, the QA team was also unable to review the analysis of selected samples for oxydemeton-methyl.

Please contact me, if you have any questions.

cc: Catherine Cooper, CDFA  
Matt Hengel, TAL  
Susan Kegley, Pesticide Action Network  
Mathew Plate, U.S. Environmental Protection Agency, Region 9  
Kathy Orr, DPR  
Lynn Baker, Air Resources Board  
Don Fitzell, Air Resources Board